D. Picking up some Formal Quantum Mechanics

(i) Inspect $\{\psi_n(x)\}$ of $\hat{H}\psi_n = E_n\psi_n$ for 1D box

Recall:
$$\psi_n(x) = \begin{cases} \sqrt{\frac{2}{a}}\sin\left(\frac{n\pi x}{a}\right), & 0<x<a \\ 0, & x\leq 0 \; \& \; x\geq a \end{cases} \qquad E_n = \frac{n^2\pi^2\hbar^2}{2ma^2}$$

They are orthogonal! (正交的)

This statement is about the set of eigenfunctions of $\hat{H}$

$\{\psi_1, \psi_2, \ldots, \psi_n, \ldots\}$ (infinitely many of them)

To define orthogonality, formally we need a way to "put two functions together".

Recall: In considering normalization, we consider the integral

$$\int_{-\infty}^{\infty} |\psi_n(x)|^2 \, dx = \int_{-\infty}^{\infty} \psi_n^*(x) \; \psi_n(x) \, dx$$

- Motivated by intensity in light
- We chose $\psi_n(x)$ to be real in 1D box, it is actually up to a phase, using $\psi_n^* \psi_n$ is more formal

To consider orthogonality, we consider the integral

$$\int_{-\infty}^{\infty} \psi_i^*(x)\, \psi_j(x)\, dx$$

(formally defines an <u>inner product</u> between functions)

different energy eigenfunctions

In QM, we need to consider complex wavefunctions in general. This integral is suitable for the purpose.

Applying this to $\{\psi_n(x)\}$ of 1D Box, for $n \neq m$

$$\int_{-\infty}^{\infty} \psi_n^*(x)\, \psi_m(x)\, dx = \frac{2}{a}\int_0^a \sin\left(\frac{n\pi x}{a}\right) \sin\left(\frac{m\pi x}{a}\right) dx = 0 \quad (n \neq m)$$

Can see this pictorially or mathematically

$\therefore$ We have $\int_{-\infty}^{\infty} \psi_n^*(x)\, \psi_m(x)\, dx = 0$ for $n \neq m$

This is what "Energy eigenfunctions are <u>orthogonal</u>" meant.

> Remark: We saw this property explicitly among the energy eigenfunctions of particle-in-a-1D-box. **The property is, in fact, general.**

Examples:

- Different energy eigenfunctions of 1D harmonic oscillator are orthogonal
- Hydrogen atom – different "atomic orbitals" (what you call 1s, 2s,…,3d,…) can be made orthogonal to each other

Why is it called "orthogonal"? (Analogy to vectors in 3D)

Consider <u>unit vectors</u> in x-direction $\hat{i}$, y-direction $\hat{j}$, z-direction, $\hat{k}$

These unit vectors are orthogonal to each other

Meaning: $\hat{i} \cdot \hat{j} = \hat{i} \cdot \hat{k} = \hat{j} \cdot \hat{k} = 0$

$$\underbrace{\hat{i} \cdot \hat{j}}_{\text{for vectors}} \text{ is the equivalence of } \underbrace{\int_{-\infty}^{\infty} \psi_i^*(x)\, \psi_j(x)\, dx}_{\text{for functions}}$$

(inner products in two cases)

[This is a useful analogy that can be carried out further, see later]

Orthonormal set of eigenfunctions (正交歸一)

Together with normalization $\int_{-\infty}^{\infty} \psi_n^*(x)\, \psi_n(x)\, dx = 1$,

same

the $\boxed{\text{ortho}}$gonal and $\boxed{\text{normal}}$ized properties

$\{\psi_1, \psi_2, \cdots, \psi_n, \cdots\}$ is a set of orthonormal functions

Meaning: $$\int_{-\infty}^{\infty} \psi_i^*(x)\, \psi_j(x)\, dx = \delta_{ij} = \begin{cases} 0 & i \neq j \\ 1 & i = j \end{cases}$$ Kronecker delta function

> Key point: TISE solutions (energy eigenfunctions) have nice properties. They form a set of orthonormal functions.

Extension: $\hat{A}\phi_n = a_n \phi_n$

$$\int_{\text{all space}} \phi_i^* \, \phi_j \, dx = \delta_{ij}$$

To convey key QM concepts, we will use this form of orthonormal relationship[†] between eigenfunctions.

† As mentioned, there are eigenfunctions that cannot be normalized. In such cases, other "normalization" criterion is invoked and typically the Dirac δ-function enters into the relationship instead of the Kronecker δ-function.

(ii) Expand any wavefunction in terms of Energy Eigenfunctions

Analogy: $\hat{i}, \hat{j}, \hat{k}$

Any vector $\vec{V}$ in 3D

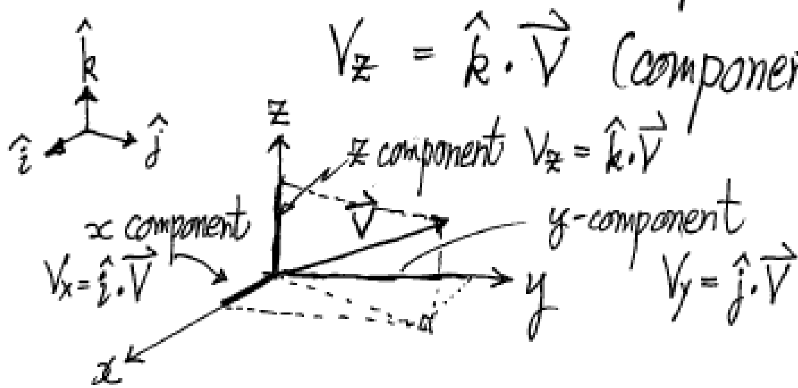
$$\vec{V} = V_x \hat{i} + V_y \hat{j} + V_z \hat{k}$$

with

$$V_x = \hat{i} \cdot \vec{V} \quad \text{(component in } x\text{)}$$

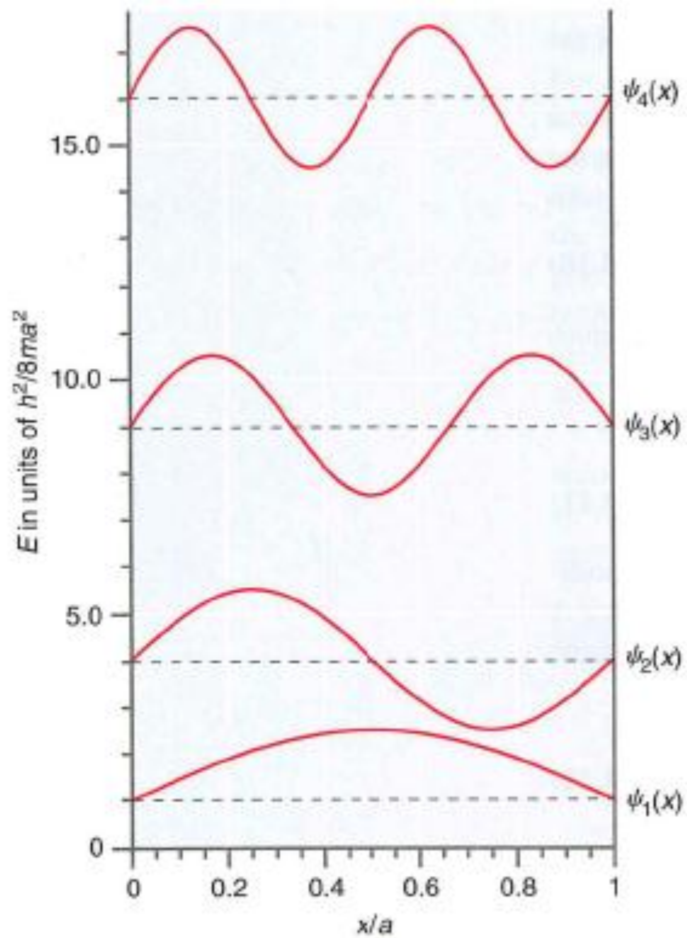
$$V_y = \hat{j} \cdot \vec{V} \quad \text{(component in } y\text{)}$$

$$V_z = \hat{k} \cdot \vec{V} \quad \text{(component in } z\text{)}$$



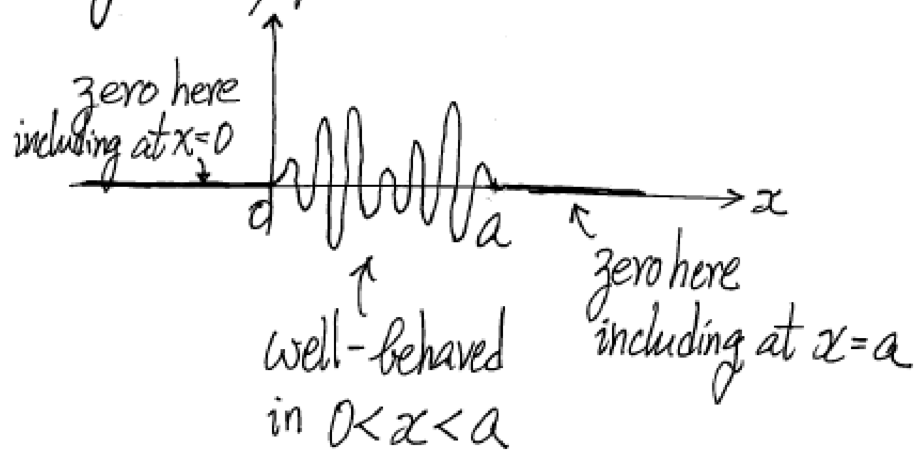
Inspect 1D Box $\psi_n(x)$'s

and infinitely many more…



Any function that is compatible with the problem (or set $\{\psi_1, \ldots, \psi_n, \ldots\}$)

Meaning: "Any" function $\Phi(x)$



Can be expressed as

$$\Phi(x) = \sum_{n=1}^{\infty} c_n \psi_n(x)$$

$$\underset{\text{Given a form}}{\Phi(x)} = \sum_{n=1}^{\infty} c_n \underbrace{\psi_n(x)}_{\text{known after solving TISE}} \quad \text{can always be done}$$

- Left multiply by $\psi_m^*(x)$ [one of $\{\psi_1, \cdots; \psi_n, \cdots\}$ and complex conjugate it]
- Integrate over all space

$$\int_{-\infty}^{\infty} \psi_m^*(x)\, \Phi(x)\, dx = \sum_{n=1}^{\infty} c_n \int_{-\infty}^{\infty} \psi_m^*(x)\, \psi_n(x)\, dx \underset{\text{orthonormal}}{=} \sum_{n=1}^{\infty} c_n \delta_{mn} \underset{\text{Definition of } \delta \text{ fn}}{=} c_m$$

$\therefore$ You give me a form $\Phi(x)$, the expansion can always be done by choosing the <u>expansion coefficients</u> c_n to be

$$c_n = \int_{-\infty}^{\infty} \psi_n^*(x)\, \Phi(x)\, dx \qquad \text{Done!}$$

The idea is closely related to that of expressing vectors in terms of unit vectors

Analogy

$$\vec{V} = (\hat{i}\cdot\vec{V})\hat{i} + (\hat{j}\cdot\vec{V})\hat{j} + (\hat{k}\cdot\vec{V})\hat{k}$$
$$= V_x\,\hat{i} + V_y\,\hat{j} + V_z\,\hat{k}$$

$$\vec{V} = \sum_{\alpha=i,j,k} \underbrace{(\hat{\alpha}\cdot\vec{V})}_{\text{component}}\,\hat{\alpha}$$

unit vector

y-component of $\vec{V}$

$\hat{j}\cdot\vec{V}$ "projecting $\vec{V}$ onto axis along $\hat{j}$"

dot product (inner product) of basis (unit) vector $\hat{j}$ and $\vec{V}$

$$\Phi(x) = \sum_{n=1}^{\infty} c_n\,\psi_n(x)$$
$$= \sum_{n=1}^{\infty}\left(\int_{-\infty}^{\infty}\psi_n^*(x)\,\Phi(x)\,dx\right)\psi_n(x)$$

"Component" of $\Phi(x)$ along "axis" defined by $\psi_n(x)$ is

$$\int_{-\infty}^{\infty}\psi_n^*(x)\,\Phi(x)\,dx$$

inner product of basis function and $\Phi(x)$

It projects $\Phi(x)$ onto "axis" along $\psi_n(x)$.

Introducing a name: "Completeness" (完備)

When an expansion $\Phi(x) = \sum_{n=1}^{\infty} c_n \psi_n(x)$ can be done

FOR ANY $\Phi(x)$.

$\{\psi_1(x), \cdots, \psi_n(x), \cdots\}$ is called a <u>complete set</u>.

So, <u>ALL</u> energy eigenfunctions form a complete set

must include All of them

Summary

TISE gives $\{\psi_n(x)\}$ and E_n

Any function can be expanded as $\Phi(x) = \sum_{n=1}^{\infty} C_n \psi_n(x)$ (1)

and C_n's are given by $C_n = \int_{-\infty}^{\infty} \psi_n^*(x)\, \Phi(x)\, dx$ (2)

With Eq.(1) and Eq.(2), we can answer initial value problems, because each component $C_n \psi_n(x)$ evolves as $C_n e^{-iE_n t/\hbar}$ in time (see Ch. III)

Mathematically, this is analogous to expressing vectors AND doing Fourier analysis

Extension: QM operator $\hat{A}\,\phi_n = a_n\,\phi_n$ (not necessarily $\hat{H}$)

$\underbrace{\{\phi_1, \cdots, \phi_n, \cdots\}}_{\text{orthonormal}}$ can also be used to expand any $\Phi(x)$

$$\Phi(x) = \sum_{n=1}^{\infty} \tilde{c}_n \underbrace{\phi_n(x)}_{\text{eigenfunctions of } \hat{A}} \quad \text{with} \quad \tilde{c}_n = \int_{\text{all space}} \phi_n^*(x)\, \Phi(x)\, dx$$

E.g. If $\{\phi_i\}$ are $e^{ik_i x}$ (k_i takes on different values representing different wavelengths),

the expansion is just Fourier transforms

AND $\hat{A}$ is the momentum operator $\hat{p}$ as $e^{ik_i x}$ are eigenfunctions of $\hat{p}$